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Note

n-Butyltriphenylphosphonium dichromate: An efficient and selective oxidizing agent

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The preparation of *n*-butyltriphenylphosphonium dichromate is described. This reagent oxidizes alcohols to carbonyl compounds, thiols to disulfides and aromatic amines to azo compounds efficiently. Benzylic and allylic oximes are selectively oxidized to their corresponding carbonyl compounds in the presence of aluminium chloride.

Oxidation of organic compounds under non-aqueous and aprotic conditions is an important reaction in synthetic organic chemistry. For this purpose different chromium(VI) based oxidants are reported in the literature[1-4]. However, some of the reported reagents suffer from disadvantages such as instability, hygroscopicity, low selectivity, long reaction time, difficulty of preparation, high cost and the need for a large excess of the reagent. Thus a milder, more selective and inexpensive reagent is still in demand.

In this paper we report the use of *n*-butyltriphenylphosphonium dichromate, a yellow-orange solid, for the effective oxidation of different classes of organic substrates in refluxing chloroform. This reagent is prepared very easily by addition of chromium trioxide in 3 *N* hydrochloric acid to a solution of *n*-butyltriphenylphosphonium bromide in water/acetone (10/1). This oxidizing agent is soluble in acetonitrile, chloroform, acetone and dichloromethane, slightly soluble in benzene and insoluble in carbon tetrachloride and diethyl ether. The experimental and calculated chromium contents of the reagent are in very good agreement. The infrared spectrum (KBr) shows bands at 960, 900, 840, 760 and 730 cm^{-1}, which are characteristic of the dichromate ion[5].

Primary and secondary benzylic and saturated alcohols are converted to their corresponding aldehydes and ketones in high yields (Table I, Entries 1-9). Further oxidation of aldehydes to their carboxylic acids were not observed. Under the same reaction conditions, primary and secondary allylic alcohols are selectively oxidized to their α,β-unsaturated carbonyl compounds without the cleavage of carbon-carbon double bonds (Table I, Entries 10-15). In contrast, manganese dioxide which has been widely used for the oxidation of allylic alcohols, requires a large excess of the reagent and long reaction times for successful oxidations[6]. Aromatic amines are converted to their azo compounds in good yields (Table I, Entries 16-21). The mildness of the reagent is shown by the oxidation of different thiols to their disulfides in excellent yields (Table I, Entries 22-26). Benzylic and allylic oximes are selectively converted to their corresponding carbonyl compounds with *n*-butyltriphenylphosphonium dichromate in the presence of 0.5 mole ratio of $AlCl_3$. Oxidation of aliphatic oximes with this reagent is not promising (Table I, Entries 27-36). In Table II some of the results of our experiments are compared with some of those reported with barium manganate[7] and tetrabutylammonium chlorochromate[8].

In conclusion, *n*-butyltriphenylphosphonium dichromate is a mild, selective and inexpensive reagent and can be prepared very easily and cheaply from commercially available materials. Therefore, this reagent which is a good oxidant is readily available for synthetic purposes in organic chemistry.

Experimental Section

General. All of the starting materials used in this work were commercially available or prepared by standard literature procedures[9]. Oxidation products were identified by comparison with authentic samples (IR, NMR, m.p.). Melting points were determined using a Mettler FP5 apparatus and are uncorrected. IR spectra were recorded on a Philips PU9716 spectrophotometer and ^1H NMR in $CDCl_3$ on a Bruker AW 80MHz spectrometer using TMS as an internal standard. GLC analysis was

Table I- Oxidation of organic compounds with $(n\text{-}BuPPh_3)_2Cr_2O_7$ in refluxing $CHCl_3$

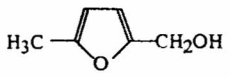
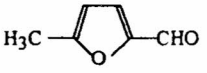
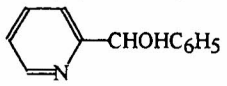
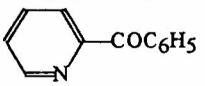
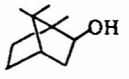
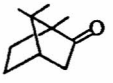
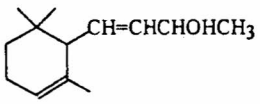
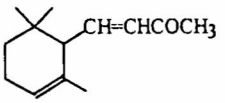
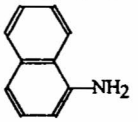
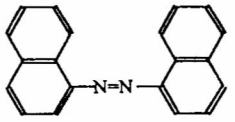
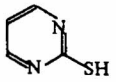
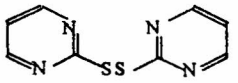
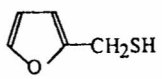
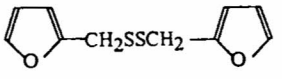
Entry	Substrate	Product	Time (hr)	Yield %
1	$C_6H_5CH_2OH$	C_6H_5CHO	0.75	100
2	$4\text{-}CH_3OC_6H_4CH_2OH$	$4\text{-}CH_3OC_6H_4CHO$	0.75	95
3			0.75	88
4	$4\text{-}ClC_6H_4CH_2OH$	$4\text{-}ClC_6H_4CHO$	1.5	95
5	$C_6H_5CHOHC_6H_5$	$C_6H_5COC_6H_5$	0.75	98
6	$4\text{-}BrC_6H_4CHOHCH_2Br$	$4\text{-}BrC_6H_4COCH_2Br$	1.5	85
7			1	90
8	$(CH_3)_2C{=}CHCH_2CH_2CHOHCH_3$	$(CH_3)_2C{=}CHCH_2CH_2COCH_3$	3.5	80
9			3	90
10	$4\text{-}CH_3OC_6H_4CHOHCH{=}CHC_6H_5$	$4\text{-}CH_3OC_6H_4COCH{=}CHC_6H_5$	1.5	85
11	$4\text{-}O_2NC_6H_4CH{=}CHCHOHC_6H_5$	$4\text{-}O_2NC_6H_4CH{=}CHCOC_6H_5$	2	80
12	$4\text{-}ClC_6H_4CHOHCH{=}CHC_6H_5$	$4\text{-}ClC_6H_4COCH{=}CHC_6H_5$	2	82
13	$C_6H_5CH{=}CHCHOHCH_3$	$C_6H_5CH{=}CHCOCH_3$	1.5	84
14			2	90
15	$C_6H_5CH{=}CHCH_2OH$	$C_6H_5CH{=}CHCHO$	1.5	92
16	$C_6H_5NH_2$	$C_6H_5N{=}NC_6H_5$	0.75	80
17	$4\text{-}CH_3C_6H_4NH_2$	$4\text{-}CH_3C_6H_4N{=}NC_6H_4(4\text{-}CH_3)$	0.75	85
18	$4\text{-}CH_3OC_6H_4NH_2$	$4\text{-}CH_3OC_6H_4N{=}NC_6H_4(4\text{-}OCH_3)$	0.75	85
19	$4\text{-}BrC_6H_4NH_2$	$4\text{-}BrC_6H_4N{=}NC_6H_4(4\text{-}Br)$	3	70
20	$3\text{-}CH_3OC_6H_4NH_2$	$3\text{-}CH_3OC_6H_4N{=}NC_6H_4(3\text{-}OCH_3)$	3	70
21			3	65
22	C_6H_5SH	$C_6H_5SSC_6H_5$	0.25	96
23	$4\text{-}O_2NC_6H_4SH$	$4\text{-}O_2NC_6H_4SSC_6H_4(4\text{-}NO_2)$	0.25	95
24			0.25	90
25			0.25	94

Table I- Continued

Table I- Oxidation of organic compounds with $(n\text{-}BuPPh_3)_2Cr_2O_7$ in refluxing $CHCl_3$

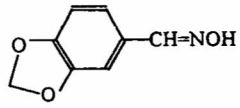
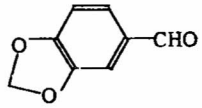
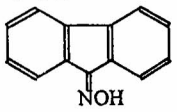
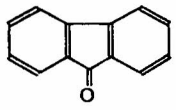
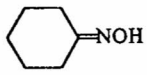
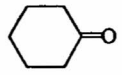
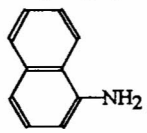
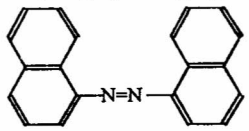
Entry	Substrate	Product	Time (hr)	Yield %
26	$(CH_3)_3CSH$	$(CH_3)_3CSSC(CH_3)_3$	0.5	90
27	$C_6H_5CH{=}NOH$	C_6H_5CHO	0.5	82
28			0.5	86
29	$4\text{-}O_2NC_6H_4CH{=}NOH$	$4\text{-}O_2NC_6H_4CHO$	0.5	70
30	$(C_6H_5)_2C{=}NOH$	$C_6H_5COC_6H_5$	0.75	85
31			0.75	75
32	$C_6H_5CH{=}CHC(NOH)CH_3$	$C_6H_5CH{=}CHCOCH_3$	0.75	70
33	$C_6H_5CH{=}CHCH{=}NOH$	$C_6H_5CH{=}CHCHO$	0.5	76
34	$C_6H_5CH{=}CHC(NOH)C_6H_5$	$C_6H_5CH{=}CHCOC_6H_5$	0.75	80
35			1	5
36	$C_6H_5CH_2C(NOH)CH_3$	$C_6H_5CH_2COCH_3$	1	0

Table II- Comparison of oxidation of some organic compounds with $(n\text{-}BuPPh_3)_2Cr_2O_7$, barium manganate ($BaMnO_4$)[7] and tetrabutylammonium chlorochromate (TBACC)[8].

Entry	Substrate	Product	Yield % (molar equiv., hr)		
			$(n\text{-}BuPPh_3)_2Cr_2O_7$	$BaMnO_4$	TBACC
1	$C_6H_5CH_2OH$	C_6H_5CHO	100 (1, 0.75)	90 (1, 0.15)	65 (3, 4)
2	$4\text{-}CH_3OC_6H_4CH_2OH$	$4\text{-}CH_3OC_6H_4CHO$	95 (1, 0.75)	-	85 (3, 7)
3	$C_6H_5CH{=}CHCHOHCH_3$	$C_6H_5CH{=}CHCOCH_3$	84 (1, 1.5)	50 (5, 3)	-
4	$C_6H_5CHOHC_6H_5$	$C_6H_5COC_6H_5$	98 (1, 0.75)	100 (2, 0.5)	82 (3, 1)
5	$4\text{-}CH_3C_6H_4NH_2$	$4\text{-}CH_3C_6H_4N{=}NC_6H_4(4\text{-}CH_3)$	85 (1, 0.75)	67 (5, 1.5)	-
6	$3\text{-}CH_3OC_6H_4NH_2$	$3\text{-}CH_3OC_6H_4N{=}NC_6H_4(3\text{-}OCH_3)$	70 (1, 3)	50 (5, 2)	-
7			65 (1, 3)	25 (5, 4.5)	-
8	C_6H_5SH	$C_6H_5SSC_6H_5$	96 (1, 0.25)	-	85 (0.5, 1)

performed with a Shimadzu 16A Gas Chromatograph with a flame ionization detector and carbowax 20M/chromosorb-W 60-80 mesh column.

Preparation of *n*-butyltriphenylphosphonium dichromate. To a solution of *n*-butyltriphenylphosphonium bromide (20 g, 5×10^{-2} mole) in water/acetone (10/1, 125 mL) was added a solution of chromium trioxide (5 g, 5×10^{-2} mole) in 3 *N* HCl (100 mL) and the mixture was stirred at room temperature for 5 min. The resulting yellow-orange solid was filtered, washed with cooled distilled water (50 mL) and dried *in vacuo*, yield 21.08 g (98.5%), m.p. 118°C (Cr%: Calc. 12.17%; Found 11.96%).

General procedure for oxidation of alcohols, amines and thiols. In a round-bottomed flask (50 mL) equipped with a condenser and a magnetic stirrer, a solution of substrate (1×10^{-3} mole) in chloroform (15 mL) was prepared and *n*-butyltriphenylphosphonium dichromate (1×10^{-3} mole) was added to this solution. The reaction mixture was stirred magnetically under reflux condition for 0.25-3.5 hr. The progress of the reaction was monitored by TLC or GLC. After completion of the reaction, silica-gel (2 g) was added and the mixture was stirred at room temperature for 10 min. The reaction mixture was filtered and the solid material was washed with chloroform (15 mL). The filtrates were combined and evaporated. The resulting crude material was purified on a silica-gel plate or silica-gel column (eluent: CCl_4/Et_2O). Evaporation of the solvent afforded pure product; yields 65-100% (Table I).

General procedure for oxidation of oximes. In a round bottomed flask (50 mL) equipped with a magnetic stirrer and a condenser, a solution of oxime (1×10^{-3} mole) in chloroform (15 mL) was prepared. *n*-Butyltriphenylphosphonium dichromate (1×10^{-3} mole) and aluminium chloride (0.5×10^{-3} mole) were added to this solution and the mixture refluxed for 0.5-0.75 hr. The progress of the reaction was monitored by TLC (eluent: CCl_4/Et_2O). After completion of the reaction, silica-gel (2 g) was added and the mixture was stirred at room temperature for 10 min. The reaction mixture was filtered and the solid material was washed with chloroform (15 mL). The combined filtrates were evaporated on a rotary evaporator and the resulting crude material was purified on a silica-gel plate or silica-gel column (eluent: CCl_4/Et_2O). Evaporation of the solvent afforded pure carbonyl compound; yields 70-86% (Table I).

Acknowledgement

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